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Some Fundamental Aspects of Solidification in a Supercooled Melt

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SOME FUNDAMENTAL ASPECTS OF SOLIDFICATION IN A SUPERCOOLED MELT

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1. INTRODUCTION

Dendritic growth in a pure melt can only occur in the presence of a negative temperature gradient in the bulk liquid ahead of the dendrite tips, in other words, in a supercooled bath since even a small positive temperature gradient in the liquid can suppress dendrite formation[1]. In an alloy melt, however, dendritic growth occurs quite readily with both positive and negative temperature gradients in the bulk liquid. This is because of the "constitutional supercooling" developing in the bulk liquid due to the compositional changes accompanying the growth process[2-4]. The main purpose of this paper is to discuss dendritic growth as it occurs in an "undercooled" or "supercooled" melt.

2. DENDRITE TIP UNDERCOOLING VERSUS BATH SUPERCOOLING

When solidification occurs in a positive temperature gradient, in an alloy melt, the temperature of the advancing solid-liquid interface (be it planar, cellular or dendritic) is always depressed below the equilibrium liquidus temperature, T_L, for the initial alloy composition, C_o, by an amount ΔT which includes the contributions due to the compositional changes occurring in the liquid, curvature, and kinetic effects[4]. During cellular or dendritic growth, this depression in the interface temperature is usually referred to as the "tip undercooling"[5,6]. It is important to recognize that steady-state cellular or dendritic growth will always occur with such an "undercooling", even if the first solid were to nucleate at exactly the liquidus temperature T_L. Likewise, if nucleation occurs after the molten alloy bath has been cooled to some temperature, T_∞, well below the liquidus, the temperature at the advancing interface will quickly rise to some value above T_∞. The temperature gradient, G_L, in the bulk liquid ahead of the advancing tips will, therefore, become negative as shown schematically in Figure 1. The temperature gradient within the interdendritic regions, G_i, may, however, be positive or negative[7]. Here it will be assumed that $G_i > 0$. Note that the dendrite tip temperature, T_t, is still depressed below T_L by an amount ΔT given by:
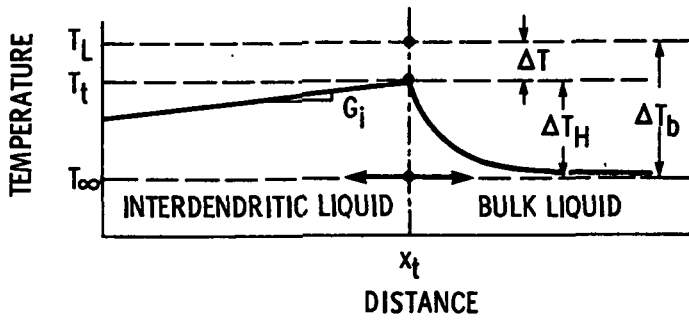
Figure 1: Temperature distribution during dendritic growth in a supercooled alloy melt.

$$\frac{\Delta T}{\Delta T_0} = \{\frac{ak}{k-1} + \frac{Rk}{D_L}(1 - \frac{ak}{k-1})\lambda_c r_t + \frac{2\ell_c k}{r_t}\} \qquad (1)$$

Here λ_c is a dimensionless quantity related to the "effective" diffusion distance δ in the bulk liquid ahead of the dendrite tips; $\delta = \lambda_c r_t$, r_t being the tip radius. The other symbols in equation have been defined in a companion paper in this volume[4]. Equation (1) above assumes that the kinetic undercooling, $\Delta T_k \simeq 0$ and that the Peclet number $p << 1/2\lambda_c(1-k)$; $p = Rr_t/2D_L$. The bulk liquid far away from the dendrite tip is depressed, below T_L, by an amount $\Delta T_b = (T_L - T_\infty)$. In what follows, ΔT_b will be referred to as the bath "supercooling". The term "undercooling" will be used exclusively to describe the depression in the tip temperature. Finally, it must be emphasized here that the dimensionless parameter $a = D_L G_i/m_L RC_0$ includes only the interdendritic temperature gradient G_i[2,3].

3. DENDRITE STRUCTURE IN A SUPERCOOLED MELT

Recent direct, in-situ, observations on dendrites growing in transparent materials such as pure succinonitrile (SCN), pivalic acid and in dilute alloys of SCN containing argon or acetone[8,9] indicate that the dendrite tip is a paraboloid of revolution with side-branches developing at a short distance behind the tip. However, this characteristic branched structure begins to degenerate to a simpler cylindrical form at moderately large bath supercoolings, whereas at very large bath supercoolings

(typically about 170 K in most ferrous alloys) there is an abrupt transition from a cylindrical to a spherical microstructure[10].
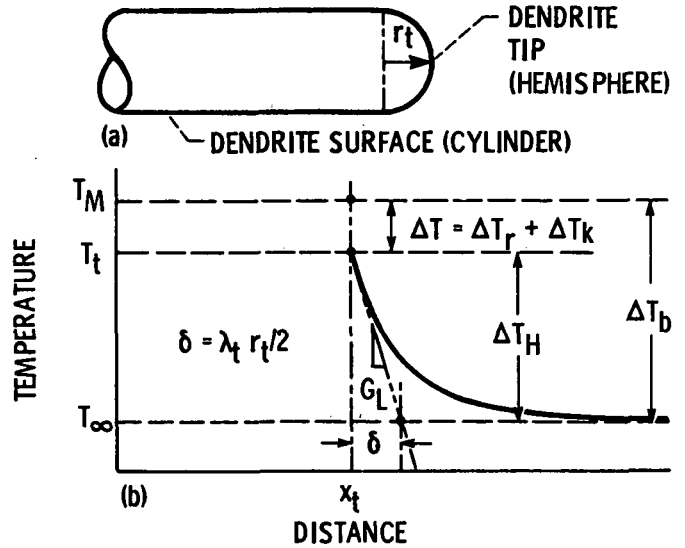

Figure 2: Dendritic growth in a supercooled pure melt.

The so-called "Fisher dendrite" which is assumed to have a hemispherical tip and a cylindrical body[11], Figure 2a, has a morphology remarkably similar to the microstructure observed in moderately supercooled melts. The solution to this dendrite shape, as it applies to a supercooled pure melt will be discussed next followed by a discussion of solidification in a supercooled alloy.

4. DENDRITIC GROWTH IN A SUPERCOOLED PURE MELT

Figure 2b illustrates schematically the temperature distribution in the bulk liquid. Let G_L be the temperature gradient in the liquid at exactly the dendrite tip. $G_L = -(T_t - T_\infty)/\delta$ where δ is now the "effective" thermal diffusion distance. This is simply the distance into the liquid at which the temperature would drop to T_∞ if the gradient in the liquid had a constant value G_L. The tip temperature T_t is depressed below the equilibrium melting point T_M by an amount $\Delta T = (T_M - T_t) = \Delta T_r + \Delta T_k$ where ΔT_r and ΔT_k are respectively the depression in tip temperature (or "undercooling")

2

attributed to the Gibbs-Thomson effect and the kinetic effect[12] associated with the growth velocity, R, of the tip. Here it will be assumed that $\Delta T_k \simeq 0$. Thus, it may be argued that only a portion, ΔT, of the total bath supercooling, ΔT_b, is required to ensure that the dendrite tip is in "equilibrium" with the bath. The remainder, ΔT_H, is required to dissipate the heat of fusion generated at the tip. A simple heat balance at the tip gives:

$$T_t = T_\infty + \frac{L}{C_p}\left(\frac{\lambda_t R r_t}{2\alpha_L}\right) \qquad (2)$$

where L is the heat of fusion per unit volume, C_p is the volumetric specific heat of the liquid, α_L is the thermal diffusivity of the liquid and $\delta = \lambda_t r_t/2$.

For equilibrium, the tip temperature must also be given by:

$$T_t = T_M - \frac{L}{C_p}\left(\frac{2d_o}{r_t}\right) \qquad (3)$$

where d_o is a characteristic length called the capillary length[8]. Combining equations (2) and (3) above yields

$$\Delta\theta = \frac{T_M - T_\infty}{L/C_p} = \lambda_t\left(\frac{Rr_t}{2\alpha_L}\right) + \frac{2d_o}{r_t} \qquad (4)$$

Figure 3 plots schematically the tip temperatures given by equations (2) and (3) respectively as a function of the tip radius. Clearly, steady-state solidification can only occur when the tip radius has the value r_1 or r_2 given by the intersection of these two plots. These radii are given by the following quadratic expression for r_t:

$$r_t^2(R/R_m) - 4R_c r_t + 4r_c^2 = 0 \qquad (5)$$

where $r_c = 2d_o/\Delta\theta$ is the critical nucleation radius[13,14] and $R_m = \alpha_L d_o/\lambda_t r_c^2$. For $R > R_m$, the roots of the above quadratic equation become imaginary. R_m is thus the maximum
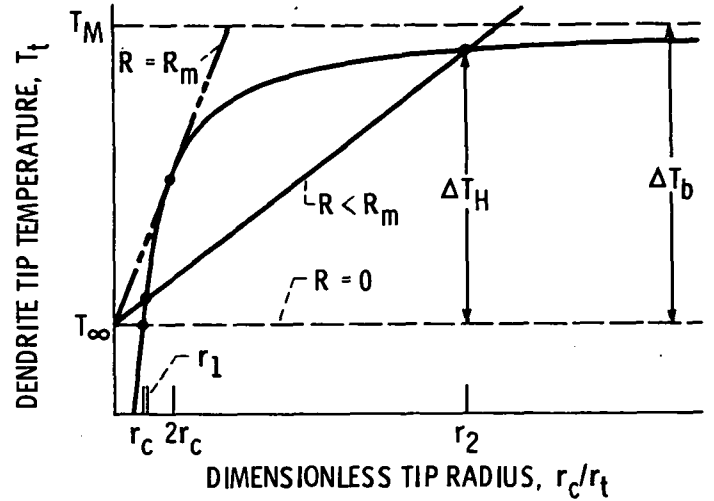

Figure 3: Schematic plot of tip temperature versus tip radius given by equations (2) and (3).

possible growth rate, for a given ΔT_b. Previous analyses have simply assumed that the dendrite grows at this maximum growth rate[8,12], for which the tip radius $r_t = 2r_c$ and the tip temperature $T_t = (T_M + T_\infty)/2$. Thus, for $R = R_m$, $\Delta T = \Delta T_H$; so that exactly one-half of the total bath supercooling ΔT_b is required to dissipate the heat of fusion.

Figure 3 clearly illustrates that the "maximum velocity" hypothesis has no firm basis and that steady-state growth can occur at a growth rate $R < R_m$. However, it is not immediately obvious what dictates the choice between the two possible radii r_1 and r_2. Rewriting equation (5) as follows:

$$\sigma = \frac{2\alpha_L d_o}{Rr_t^2} = \frac{\lambda_t}{2}\left(\frac{r_t}{r_c} - 1\right)^{-1} \qquad (6)$$

Here σ is a dimensionless parameter characteristic of the dendritic growth process[14]. For $R \ll R_m$, this parameter, for the larger radius r_2 given by equation (5) is approximately equal to

3

$$\sigma \simeq \frac{\lambda_t}{8} \left(\frac{R/R_m}{1-R/4R_m} \right) \tag{7}$$

and, for the smaller radius r_1, $\sigma \simeq -\lambda_t/2$. For $R = R_m$, σ is exactly $\lambda_t/2$.

It is important to note here that the parameter σ obtained here is exactly the "tip stability" parameter obtained by Langer and Muller-Krumbhaar[14]. σ follows naturally from the analysis of steady-state solidification as discussed here. It may be calculated simply by knowing either the dendrite tip growth rate, R, or the tip radius, r_t, provided λ_t is known. It has usually been assumed that $\lambda_t \simeq 1$ but this need not be true[3,4]. Thus, for pure SCN[15], the measured tip radius at $\Delta\theta = 0.001$ is about 30 μm and the observed growth rate R = 10 μm/sec. At this supercooling, $r_c = 0.54$ μm and $R_m = 1037/\lambda_t$ m/sec, giving $\lambda_t \simeq 7.466$. Thus, the "effective" thermal diffusion distance is almost four times the tip radius at this supercooling.

Langer and Muller-Krumbhaar observed that for σ greater than a critical value, σ^*, side-branching along the dendrite surface greatly decreases. Thus, it may be argued that "cylindrical" (and also, "spherical") growth morphology observed in moderately supercooled melts correspond to dendritic growth with large values of σ. This simply implies that dendritic growth will occur at smaller values of the ratio r_t/r_c with increasing bath super-coolings.

5. DENDRITIC GROWTH IN A SUPERCOOLED ALLOY MELT

In an alloy melt, steady-state solidification will occur with a tip radius which satisfies both equations (1) and (2) simultaneously:

$$\frac{\Delta T_b - am_L C_0}{\Delta T_0} = 2\lambda_c\beta k(1+\xi) \frac{Rr_t}{2D_L} + \frac{2\ell_c k}{r_t} \tag{8}$$

where
$$\xi = \frac{D_L\lambda_t/2}{\lambda_c\beta k\alpha_L\Delta T_0(C_p/L)} \tag{9}$$

and $\beta = 1 - ak/(k-1)$. In metal alloys, D_L/α_L is typically about 10^{-3}, so that, ξ is negligibly small, especially at large growth rates for which $\beta \simeq 1$ since $a \simeq 0$. Thus equations (4) and (8) are remarkably similar if $a \simeq 0$ and $\xi \simeq 0$ with λ_t, α_L and d_0 being replaced by their chemical counterparts λ_c, D_L and ℓ_c. For a pure metal the partition ratio $k = 1$. Note that $a \simeq 0$ both for very large growth rates and also if the interdendritic concentration gradient, G_i/m_L, is negligibly small[3]. Thus it may be argued that $a \simeq 0$ when spherical particles grow in a supercooled alloy melt, since within a spherical particle there are no "interdendritic channels" through which solute diffusion takes place. Equation (8) may, therefore, also be used to describe solidification in a highly supercooled melt.

Rewriting equation (8) yields a dimensionless parameter $\sigma_c = 2\ell_c D_L/Rr_t^2$, given by:

$$\sigma_c = \lambda_c(1 + \xi) \left(\frac{r^*}{r_t} - 1 \right) \tag{10}$$

where
$$r^* = \frac{D_L/Rk}{\lambda_c(1+\xi)\Delta T_0/\Delta T_b}$$

Note that σ_c is the chemical counterpart of the "tip stability" parameter σ defined earlier[16]. For $r_t > r^*$, σ_c will become negative. r^* thus represents the maximum particle size or the tip radius for a given growth rate and bath supercooling. The smallest particle size is, of course, the critical nucleation radius, r_c, which may be obtained from equation (8) directly by setting R = 0, with $\beta = 1$, $a = 0$. Thus, $r_c = 2\ell_c k\Delta T_0/\Delta T_b$, and,

$$\frac{r^*}{r_c} = \frac{D_L/2\ell_c k^2}{R} \left(\frac{\Delta T_b}{\Delta T_0}\right)^2 \frac{1}{\lambda_c(1+\xi)} \qquad (12)$$

Recall that $R_a = D_L/\ell_c k^2$ is the growth velocity above which a planar interface will remain stable according to the "absolute stability" criterion[4,17]. At these large growth rates σ_c becomes negligibly small since λ_c also tends to zero[3,4] at large values of R. This may be interpreted as implying "solute trapping" or "partitionless" solidification for which k tends to unity. More importantly, equation (10) clearly indicates that the "tip stability" parameter σ_c is the underlying fundamental quantity governing these transitions. Finally, it may be noted that the stability parameters σ and σ_c are both related to the respective dimensionless length scales λ_t and λ_c.

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16. Abstract

A model for dendritic growth in both supercooled pure and alloy melts has been presented. In a pure melt, dendrite morphology is determined by the value of the dimensionless parameter $\sigma = 2\alpha_L d_o / R r_t^2$, whereas, in an alloy melt it is determined by the parameter $\sigma_C = 2\ell_C D_L / R r_t^2$. The application of the above analysis to cylindrical and spherical growth morphologies obtained in highly supercooled melts has been discussed. An upper and lower bound for the particle or tip radius in this case has been obtained in terms of the growth rate and the initial bath supercooling.

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